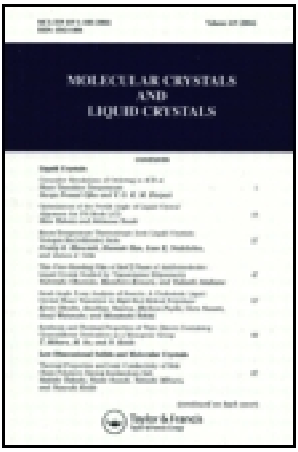

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Theoretical Calculation of Effective Exchange Integrals for One-and Two-Dimensional Poly(Phenylenemethylene) Systems. Possibilities of Organic Ferro- and Ferri-Magnetic Solids

Daisuke Yamaki [a] , Satoru Yamada [a] , Goro Maruta [a] , Takashi Kawakami [a] , Wasuke Mori [a] & Kizashi Yamaguchi [a]
[a] Department of Chemistry, Faculty of Science, Osaka University, Osaka, 560, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Daisuke Yamaki , Satoru Yamada , Goro Maruta , Takashi Kawakami , Wasuke Mori & Kizashi Yamaguchi (1996): Theoretical Calculation of Effective Exchange Integrals for One-and Two-Dimensional Poly(Phenylenemethylene) Systems. Possibilities of Organic Ferro-and Ferri-Magnetic Solids, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 279:1, 9-18

To link to this article: http://dx.doi.org/10.1080/10587259608042171

Mol. Cryst. Liq. Cryst., 1996, Vol. 279, pp. 9–18
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THEORETICAL CALCULATION OF EFFECTIVE EXCHANGE INTEGRALS FOR ONE- AND TWO-DIMENSIONAL POLY(PHENYLENEMETHYLENE) SYSTEMS. POSSIBILITIES OF ORGANIC FERRO-AND FERRI-MAGNETIC SOLIDS

DAISUKE YAMAKI, SATORU YAMADA, GORO MARUTA, TAKASHI KAWAKAMI, WASUKE MORI AND KIZASHI YAMAGUCHI
Department of Chemistry, Faculty of Science, Osaka University, Osaka 560, Japan

Abstract Ab initio post UHF, DFT, CASSCF and semiempirical INDO calculations were carried out for one- and two-dimensional poly(phenylenmethylene) in order to elucidate variations of the effective exchange integrals with molecular connectivity, cluster size and hole (electron) doping. It was shown that the ferromagnetic effective exchange integrals by UCCSD(T) and DFT/4-31G are about 400 cm^{-1} for m-phenylene bis(methylene). The high-spin ground states of hole-doped polycarbenes were also studied, indicating a possibility of obtaining the high T_c organic ferrimagnets induced by the one electron transfer between polycarbene and spacer (electron donor or acceptor).

INTRODUCTION

Previously [1], unrestricted Hartree-Fock (UHF) molecular orbital (MO) and post UHF calculations have been carried out for an elucidation of through-bond couplings between carbene groups. Computational results have indicated that the spin plarization (SP) rule is applicable to qualitative explanations of the ground spin states of one-dimensional (1D) neutral polycarbenes. On the other hand, the spin delocalization (SD) mechanism is found to be operative in the case of hole doped polycarbene systems [2,3]. Recently Iwamura [4] and Itoh-Takui [5] groups reported the synthesis of two-dimensional (2D) polycarbene systems which may exhit so-called superparamagnetism. In the present paper we first investigate the 1D phenymethylene oligomers in order to elucidate the dependence of the effective exchange integrals (J_{ab}) on the oligomer size. We also investigate the 2D neutral polycarbenes and hole-doped phenyl tris(methylene) in relation to recent experiments [4, 5]. For the purpose, we will perform the first principle density functional (DFT), post UHF, UNO CASSCF, UNO CAS-CI [3] and semiempirical (INDO) calculations of these 1D- and 2D-systems in order to elucidate variations of J_{ab} with the cluster size and hole doping. The expansion of the dimensionality is a well-known approach to bulk ferromagnets [4-6]. Since the intrachain effective exchange integrals converge to a saturated value and the interchain interactions are usually weak [7], we will propose the other strategy to obtain ferrimagnetic organic solids generated by one electron-transfer between polycarbene and spacer group (donor or acceptor) [6].

TWO SITE MODELS

(A) Comparison between ab initio post UHF and DFT methods

First of all, let us examine the effective exchange integrals for meta(m) and para(p) phenylene bis(methylene) by ab initio post UHF methods with their optimized geometries obtained by the UHF/4-31G energy gradient procedure presented previously [1]. The details of the computational methods are given elsewhere [1,3]. Table 1 summarizes the calculated J_{ab} values for meta- and para- phenylene bis(methylene). From Table 1, the following conclusions are drawn:

(1) All the calculated J_{ab} values for meta-phenylene-bridged bismethylene (**1**) are found to be positive in sign (ferromagnetic), while the J_{ab} values for para-phenylene-bridged bismethylene (**2**) are negative (antiferromagnetic). This result is in good agreement with the predictions by molecular connectivity [5], valence-bond (VB) model and spin polarization (SP) rule [1, 2].

(2) The J_{ab} value by the UHF coupled-cluster (CC) single and double excitation (UCCSD) method is 704 cm^{-1} for **1**, whereas it is reduced to 402 cm^{-1} by the perturbation correction including the triple excitation (T) in the UCCSD(T) scheme.

(3) The J_{ab} values for **1** by the unrestricted Kohn-Sham (UKS) Becke (B) or Slater (S)-Lee-Yang-Parr (LYP) methods, UKS B(S)-LYP [8], are close to the UCCSD(T) value.

(4) The J_{ab} values by approximately spin-projected (AP) but size-consistent UHF (APUHF)/4-31G and INDO for **1** are larger, respectively, by six and four times than the UCCSD(T) value. This tendency is the same as shown in the case of small polycarbenes previously [1].

(5) Absolute values of J_{ab} by UCCSD, UCCSD(T) and UKS B(S)-LYP are quite similar for **2**, but the corresponding values by APUHF /4-31G and INDO are about twice of the UCCSD(T) value.

From these results, it is found that the DFT method can reproduce the J_{ab} values by UCCSD(T)/4-31G, and that the INDO method can give pretty resonable J_{ab} values, indicating the applicability to larger polycarbene systems.

Table 1 $Jab^{d)}(cm^{-1})$ values for phenylene bis (methylene) by the post UHF methods

Method	meta$^{a)}$	para$^{b)}$
UCCSD$^{c)}$	704.1	-2019.1
UCCSD(T)$^{c)}$	401.9	-1894.6
APUHF$^{c)}$	2342.1	-3753.3
APUHF INDO	1749.6	-3486.9
APUKS S-LYP$^{c)}$	316.8	-2091.2
APUKS B-LYP$^{c)}$	417.5	-1980.9

a) at the quintet optimized geometry by UHF/4 - 31G.
b) at the singlet optimized geometry by UHF/4 - 31G.
c) 4 - 31G basis set is used
d) effective exchange integral for the isotropic Heisenberg model

Table 2 $Jab^{d)}$ (cm^{-1}) values for phenylene bis (methylene) by the CI methods

Method$^{c)}$	meta$^{a)}$	para$^{b)}$
UNO CAS-CI{4,4}	188	-1992
UNO CAS-CI{8,8}	507	-1453
UNO CAS-CI{10,10}	677	-1552
UNO CAS SCF{4,4}	170	
UNO CAS SCF{8,8}	519	-1653
UNO CAS PT2{4,4}	406	

a) at the quintet optimized geometry by UHF/4 - 31G.
b) at the singlet optimized geometry by UHF/4 - 31G.
c) 4 - 31G basis set is used
d) effective exchange integral for the isotropic Heisenberg model

(B) UNO analysis and UNO CAS CI and CASSCF calculations

Although the SP rule based on the UHF approximation works well for polycarbene systems [1], the configuration-interaction (CI) type methods are also useful in order to elucidate the spin alignment mechanisms from the spin-restricted view point [3, 9]. To this end, the UHF natural orbital (UNO) analysis [10] was first conducted to determine their occupation numbers in the ground quintet state. Figure 1 illustrates the orbital symmetries and the occupation numbers of UNO. From fig. 1, they are 1.0 for two π- and two σ-SOMOs, while the occupation numbers of π^* UNO are larger than 0.1, indicating the large spin polarization effect [10]. This is consistent with the overestimation of the SP effect under the ab initio UHF approximation [1].

In order to examine the SOMO-SOMO interactions, the full configuration interactions within the four SOMOs and four electron subsystem {4,4} was performed for both the singlet and quintet states, and the effective exchange integral was calculated by the total energy difference between these states [1, 3]. The full CI were also carried out by expanding the number (m) of active UNOs and number (n) of active electrons {m,n}: {8,8} and {10, 10} include , respectively, the four π-UNOs of phenyl group in addition to the four SOMOs and all the UNOs in fig. 1. These full CI within the complete active space (CAS) are referred to as UNO CASCI [9], which incorporates the spin polarization (SP) of paired orbitals by the exchange interactions with SOMO electrons and other higher-order excitations. The UNO CASCI results are refined by the SCF procedure, leading to the UNO CASCF [3, 9, 11]. The J_{ab}-values by these refined methods were also calculated as previously [1, 3]. The results are summarized

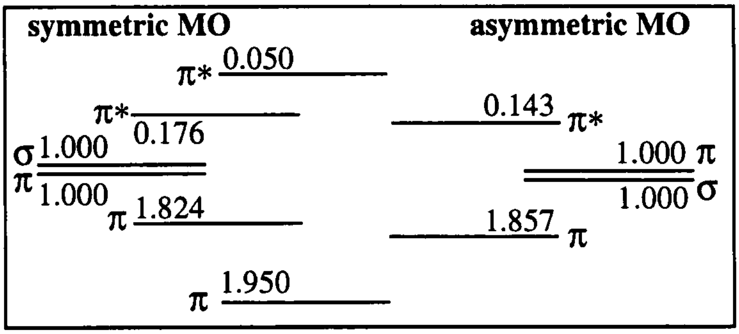


Fig.1 UHF Natural Orbitals and occupation numbers for m-phenylene bis (methylene) in the quintet state

in table 2.

From table 2, the following conclusions are drawn:

(1) The UNO CAS CI {4,4} method provides the positive J_{ab} value (about 200 cm^{-1}) for **1** , which is close to that of UNO CASSCF {4,4}. The value is responsible for the kinetic (KE) and potential exchange (PE) terms, although the KE term is almost zero because of the SOMO-SOMO orthogonality.

(2) The J_{ab} values for **1** by UN O CAS CI {8, 8} and {10,10} are larger by about two times than that of UNO CASS CI {4,4}. The former two methods include both the spin polarization (SP) and higher-order correlation correction (EC) terms in addition to KE and PE. These results are not altered even after the refinement by the CASSCF procedure.

(3) The second-order pertubation (PT2) method based on the UNO CASSCF {4,4} provides almost the same J_{ab} value for **1** by UCCSD(T).

(4) The absolute value for **2** by UNO CASCI {4,4} is not so improved by inclusion of the SP and EC terms, since the KE term via the π-SOMO-SOMO overlap is dominant in the case of para-phenylene bridged systems.

From the present analysis, it is noteworthy that the potential exchange (PE) term between SOMOs is indeed very important for **1** although the SP mechanism is conveniently used for simple explanation of the ferromagnetic coupling of carbebe groups in a previous paper [1]. On the other hand, the spin delocalization (SD) effect is important for hole-doped bismethylene systems as shown previously [1, 3].

VARIATIONS OF EFFECTIVE EXCHANGE INTEGRALS WITH CLUSTER SIZES

(A) Calculations of J_{ab} values of N-site oligomers

In order to examine the cluster size-dependency of J_{ab}, the J_{ab} values for the N-site one-dimension (1D) systems are calculated under the assumption that (1) the overlaps between SOMOs are not so large and (2) therefore the Heisenberg (HB) model can be used for through-bond exchange couplings between triplet methylene sites. The J_{ab} values were easily calculated by the combinations of the UHF (or UKS) MO method plus HB model under the assumption of the uniform 1D magnetic chain with one J_{ab} as

$$J_{APUHF} = \frac{{}^{HS}E_{UHF} - {}^{LS}E_{UHF}}{{}^{HS}\langle S^2 \rangle - {}^{LS}\langle S^2 \rangle - \Delta}, \qquad (1)$$

where

$$\Delta = \begin{cases} (N-2)^2/4 & \text{if } N\text{:even} \\ (N-1)(N-3)/4 & \text{if } N\text{:odd} \end{cases} \qquad (2)$$

It is noteworthy that the present approximate spin projection (AP) scheme for UHF (or UKS) is size-consistent, guaranteeing the necessary condition for theoretical studies of extended systems [1]. Here, the INDO parameter was used for the oligomers for computational economy, although ab initio UKS B-LYP method was desirable, as can be recognized from table 1, for semi-quantitative discussions of the effective exchange interactions in the polycarbene systems.

Eqs. 1 and 2 were applied to elucidate the dependence of J_{ab} values on the oligomer size N in the case of para- and meta-phenylene bridged oligomers. Figure 2 illustrates two different molecular structures with terminal hydrogen and phenyl groups. Figures. 3 and 4 illustrate variations of J_{ab} with N for both types of polycarbene systems. From figs.3 and 4 , it is clear that the absolute values of J_{ab} values for polycarbenes with terminal phenyl groups increase with the increase of the oligomer size N ,while the absolute values of J_{ab} values for polycarbenes with terminal hydrogen atoms decrease with the increase of N. However, both the J_{ab} values converge to each saturated values even at $N \approx 10$. The estimated J_{ab} values at $N = \infty$ are 850 ~ 880 cm^{-1} for meta-phenylene-bridged oligomers, whereas they are -1530 ~ -1550 cm^{-1} for para-phenylene-bridged oligomers. Judging from the conclusions (4) and (5) for m(p)-phenylene bis(methylene) **1** and **2**, the J_{ab}-values for the former and latter oligomers are estimated to be about 220 and -700 cm^{-1}, respectively. These theoretical values are consistent with several experimental results [12,13].

Figure 5 illustrates the spin density populations on the central phenylene bis(methylene) group for the m-phenylene- and the p-phenylene-bridged models with the moderate size N=11 by the INDO UHF method. The spin density populations are

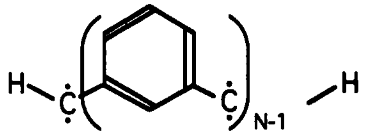
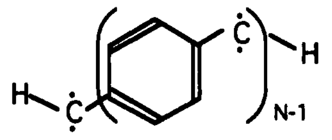
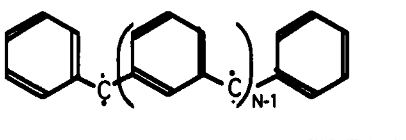
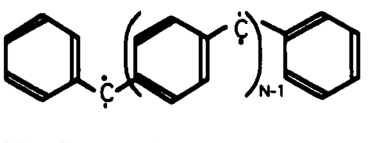
	meta-phenylene bridged system	para-phenylene bridged system
with terminal hydrogen atoms		
with terminal phenyl groups		

Fig.2 Molecular structures of 1D poly carben systems

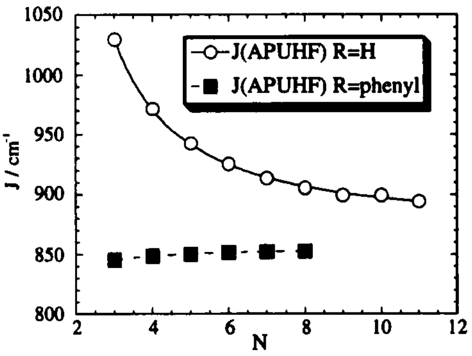


Fig.2 J vs cluster size N for Poly- meta-phenylene-methylenes [R-C-(m-phenylene-C)$_{N-1}$-R]

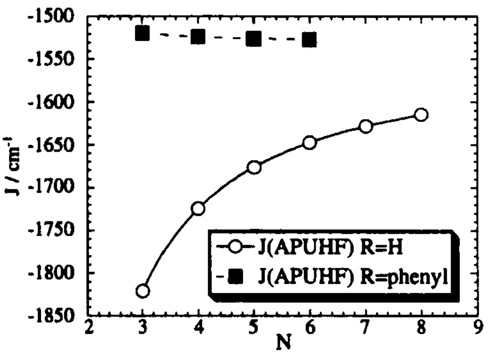


Fig.3 J vs cluster size N for Poly- para-phenylene-methylenes [R-C-(p-phenylene-C)$_{N-1}$-R]

alternating like a spin-density-wave (SDW) and are useful for pictorial understanding of the intramolecular spin alignment rules via the SP effect. However, it is noteworthy that the SOMO-SOMO potential exchange, together with the electron correlations responsible for the higher-order exchange interactions, also plays an important role in polycarbene systems.

TWO-DIMENSIONAL (2D) POLYCARBENES

(A) Ab initio calculations of tris(methylene) benzene

Since the neutral and hole-doped states of phenyl bis(methylene) systems have been examined in detail [3], we present a new result on the hole-doped tris(methylene) benzene 3 for later discussions. Table 3 summarizes the total and relative energies

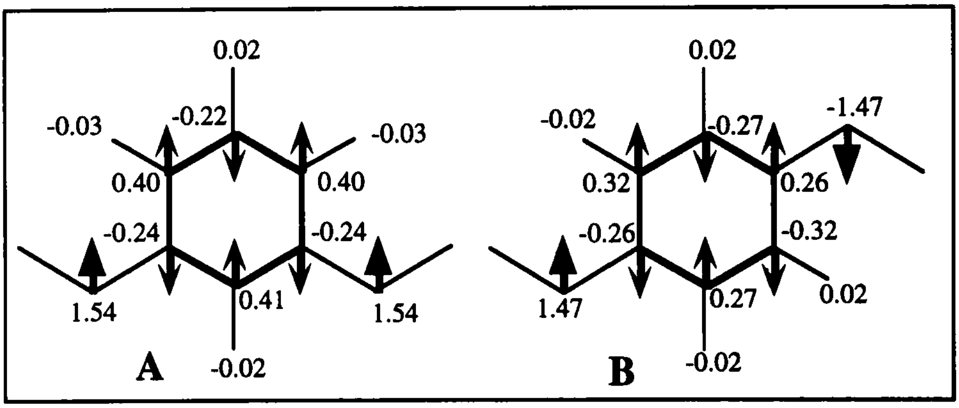


Fig.4 Spin densities for m(A)- and p(B)- poly (phenylene-methylene)s

obtained for four different spin states of 3^+ by UNO CASSCF/4-31G by the use of the eight active UNOs and seven-active electrons {8,7}. The high-spin sextet state (S=5/2) is the ground state of 3^+, indicating that the π-SOMO electron is extracted upon hole-doping and the ground spin state is given by S=(3x2 -1)/2. This situation is the same for hole-doped 1D polycarbene systems [1-3].

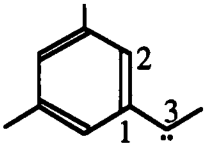
Table.3 UNO-CASSCF[8,7] calculations of π-hole doped trimethylene phenylene

2S+1	Etotal	ΔE(rel.)[a]
2	-343.1769	3.37
4	-343.2790	0.592
6	-343.3008	0.0
8	-343.2270	2.01

a) relative energies(eV) in parentheses

Table.4 Spin Densities for 2D poly carbene 4 (M=1~3) by the INDO UHF

M	1	2	3
1	-0.273	0.558	1.540
2	-0.272	0.547	1.534
3	-0.272	0.548	1.534



(B) 2D polycarbenes

The present calculations indicate the saturation phenomena of the intramolecular J_{ab} values for one-dimensional polycarbene systems. Although these linear polycarbenes are particularly interesting as quantum spin systems, two- or three-dimensional molecular skeletons are necessary to realize the macroscopic organic ferromagnetism by the use of triplet carbene units [1, 7]. In fact, several groups initiated such experimental efforts to synthesize two-dimensional (2D) polycarbene systems **4** shown in fig. 6 [4, 5]. Here, we carried out the INDO UHF calculations [10] of the 2D polycarbenes **4** with the side chain lengths M=1-3. Table 4 summarizes the spin densities on the key carbon atoms of **4**. As an example, the spin density populations of

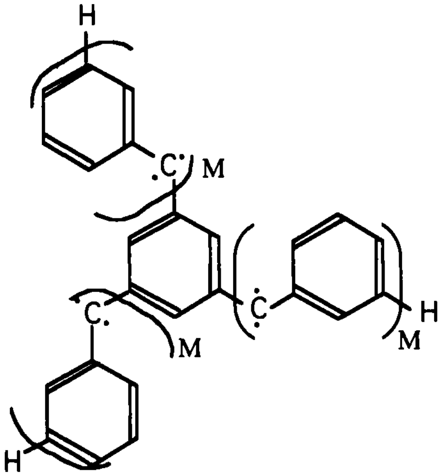


Fig.6 Molecular structures of 2D poly carbens **4**

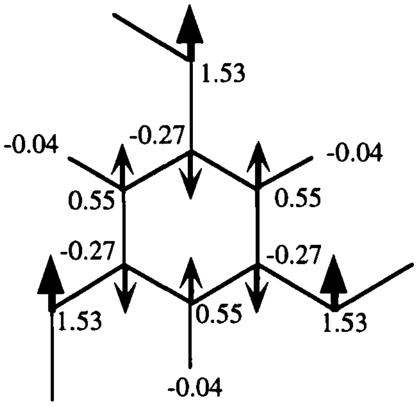


Fig.7 Spin densities for **4** (M=3) by the INDO

the central tris(methylene) benzene embedded in **4** (M=3) are shown in fig. 7. From fig. 7, it is clear that the spin correlation is operative in constructive manner to stabilize the high-spin ground state with the spin multiplicity S=9. Although 2D polycarbenes with M> 2 have not been synthesized yet [4, 5], these will become potential units for real 3D organic ferromagnets if interplane or interchain interactions can be controlled to be ferromagnetic.

DISCUSSIONS

(A) Interchain effective exchange interactions

In a previous paper [14], we have throughly investigated the intermolecular effective exchange interactions between triplet phenylcarbenes. It was shown that the intermolecular spin-polarization rules are applicable to estimate the sign of the intermolecular J_{inter} values [1, 7, 14]. However, the magnitudes of the ferromagnetic J_{inter} values are usually small even for phenylcarbene systems with large spin polarization effects. Therefore, it seems difficult to obtain the high-T_c (>77 K) organic ferromagnetic crystals. In fact, the crystalline organic ferromagnets composed of nitroxide radicals exhibit the ferromagnetic phase transition at lower T_c (<1 K) [15].

(B) Possibilities of high-Tc ferrimagnetic CT solids

In order to obtain the high-T_c magnetic materials, we propose the use of strong intermolecular antiferromagnetic (weak chemical bonding) interaction between radical

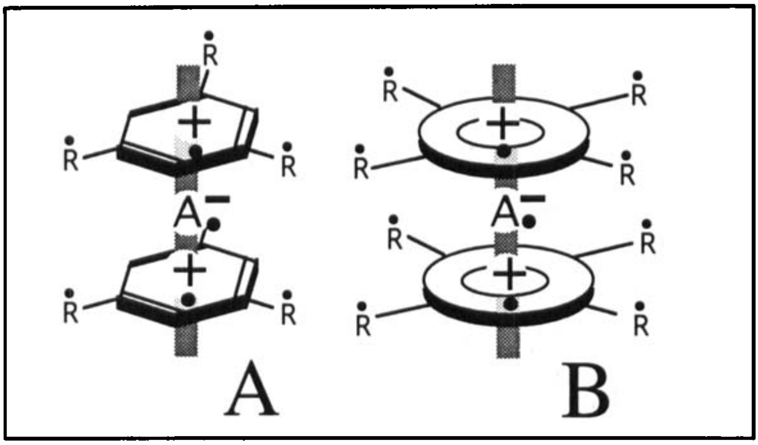


Fig.8 Possible organic ferrimagnets conposed of 2D poly carbene (A) or porphyrine skelton (B) with radical groups ($\dot{R}$)

species with different spin multiplicities, leading to concept of organic ferrimagnetism by the use of CT complexes [6]. According to this guiding principle, we carried out the computer experiments of some typical CT systems and confirmed theoretical possibilities of formations of organic ferrimagnets [6]. From this point of view, polycarbene systems linked with several π-networks (benzene ring, porphyrine ring, large aromatic compounds etc) are potential candidates for formations of organic ferrimagnetic CT solids [6]. Figure 8 illustrates possible organic ferrimagnets generated by thermal or photochemical one-electron transfers.

ACKNOWLEDGMENTS

We are grateful for the financial suport of the Ministry of Education,Science and Culture of Japan. (Specially Promoted Reserch No.06101004).

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